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OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

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SUBJECT: EFED Review of Documents Relative to Section 24c Special Local Needs Registration of Carbaryl for Use on Oyster Beds.

TO: Anthony Britten, Chemical Review Manager
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The Environmental Fate and Effects Division (EFED) has completed its review of the materials submitted relative to the Section 24c Special Local Needs registration of carbaryl for use on oyster beds in Willapa Bay and Grays Harbor, Washington, to control ghost shrimp *(Callianassa californiensis*) and mud shrimp (*Upogebia pugettensis*). The documents included **1)** a report on concentrations of carbaryl and its degradate (1-naphthol) in marine sediments from sites treated with or adjacent areas treated with Sevin (Stonic 1999); **2)** a fact sheet on chemicals of special concern in Washington State; **3)** a memo from the State of Washington's Department of Ecology's review of data relevant to the environmental effects of applying Sevin™ to control burrowing shrimp in Willapa Bay and Grays Harbor oyster beds; **4)** a copy of the memorandum of agreement between the Washington State Department of Ecology, the Willapa/Grays Harbor Oyster Growers' Association and other state government and private organizations; and **5)** a Washington State Department of Ecology publication entitled Carbaryl Concentrations in Willapa Bay and Recommendations for Water Quality Guidelines (Johnson 2001). Except for more recent studies conducted by Washington State University and the Washington Department of Ecology, much of the older (pre-1996) data had procedural problems that limited the utility of the data. The more recent data indicate that carbaryl residues in the water column were generally at or below an effect threshold of 0.1 ug/L Although large carbaryl applications can affect water quality in areas distant from spray sites, the Washington Department of Ecology concluded that "no widespread effects from carbaryl would be expected in Wallapa Bay after the end of the [carbaryl] application period."

Carbaryl has been used on approximately 600 acres of Willapa Bay and 200 acres of Grays Harbor at a rate of 7.5 to 10 lbs/acre/year since the 1960's. Carbaryl is applied as a wettable powder

to tidelands at low low [Spring] tide primarily by helicopter; however, hand spraying is used in some instances. The label restricts aerial applications within 200 feet of a channel or slough; hand spraying is prohibited within 50 feet of a channel or slough.

The data collected and/or reviewed by the Washington Department of Ecology indicate that carbaryl residues drop below the level of quantitation (< 0.004 ug/L) approximately 6 weeks after application. While concentrations in nontarget areas immediately following the carbaryl application period are likely to inflict mortality to aquatic organisms, no data are provided to demonstrate that threatened and/or endangered species (*e.g.* salmonids) are adversely affected by the treatments to oyster beds.

While these documents provide additional information on the environmental fate and effects of carbaryl in estuarine/marine environments, EFED's review of Washington's Section 24c petition was based on the required guideline fate and effects data provided by the registrant in support of the reregistration of carbaryl. Although the EFED reregistration eligibility document (RED) for carbaryl does not estimate environmental concentrations for applications directly to tidelands for control of burrowing shrimp in oyster culture, it does discuss the use. Data submitted in support of reregistration (MRID 419826-06) indicate that estuarine/marine invertebrates will likely be impacted by this route of exposure and that certain species, *e.g.*, Dungenese crab (*Cancer magister*), may experience 100% mortality in the application area. However, the assessment goes on to note that effects on aquatic invertebrates will likely be temporary as most populations show signs of recovery within 2 months. Additionally, the chapter suggests that carbaryl applications that reduce the potential for drift to nontarget sites, such as direct injection of carbaryl into the sediment, may help mitigate nontarget effects.

Review of Submitted Literature

1) Screening Survey of Carbaryl (Sevin) and 1-naphthol Concentrations in Willapa Bay Sediments

The study was undertaken to determine the long-term persistence of carbaryl and 1-naphthol; more specifically, the study objectives were to:

- Determine if there are residues of carbaryl and its degradate 1-naphthol in the marine sediments at historically sprayed sites and unsprayed adjacent sites
- Monitor the depletion of these compounds in sediments following applications of Seven™.
- Measure concentrations of carbaryl in centrifuged sediment pore water.
- Determine drift potential.

The study was divided into two phases, pre-spray and post-spray. Sampling was conducted in Willapa Bay in areas deemed to be conducive to carbaryl persistence. Thus, areas with muddy and/or fine sediments were selected since they were believed to be more likely to retain both carbaryl and 1-naphthol. Sandy sediments were not believed to provide sufficient clay or organic material with which carbaryl and/or its degradate could sorb.

Pre-spray samples were collected from areas that had been sprayed in previous years or were adjacent to areas that had been sprayed in previously. A reference site, Nemah Oyster Reserve, was sampled as an area that had never been sprayed.

Post-spray samples were collected immediately following carbaryl treatment and also included areas adjacent to spray sites. Treated sites included areas that had been sprayed in years past in addition to the recent treatment. Sampling was typically conducted 2, 30 and 60 days after treatment (DAT). Sediment samples were collected using a stainless steel 17-cm diameter device that allowed sediment samples to be stratified into 0 - 2 cm, 2 - 7.5 cm, and 7.5 - 15 cm depths. Total organic carbon (TOC) and sediment size were also analyzed. Carbaryl and 1-naphthol residues were measured both in whole sediment and in centrifuged pore water. Quality assurance spiked sediment samples suggest considerable amount of variability in recovery of standards. The results may be negatively biased.

Based on the pre-spray study results, all of the historically sprayed sites, adjacent unsprayed sites and the reference site showed no carbaryl or 1-naphthol residues above the detection limit range of 21 to 58 ppb. One sample representing the shallowest area adjacent to historically sprayed beds had trace (29 ppb) residues of carbaryl.

Post-spray study results indicate that carbaryl concentrations at sprayed sites ranged from 2,000 to 3,400 ppb by 2 DAT, 180 to 220 ppb by 30 DAT, and 86 - 120 ppb by 60 DAT (**Figure 1**). Although, adjacent sites contained as much as 2,000 ppb 2 DAT, residues in sediment at all adjacent sites at 60 DAT were close to detection limits and ranged from 27 to 32 ppb.

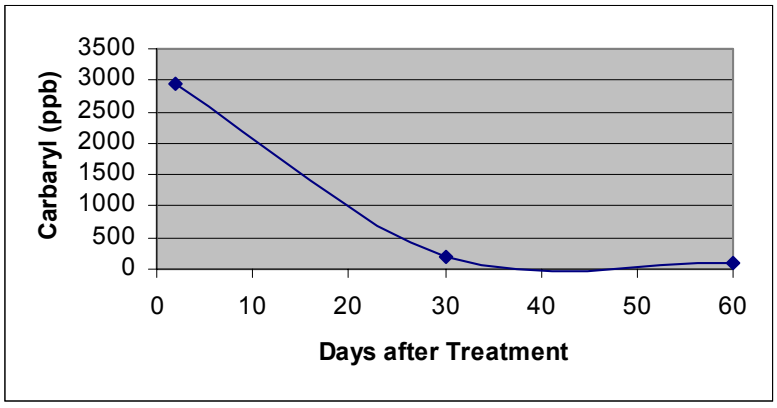

Figure 1 Average carbaryl concentrations in sediment collected from Willapa Bay at 2, 30 and 60 days after treatment.

Residues for the 1-naphthol ranged from detection limits to as high as 170 ppb at 2 DAT and by 30 DAT all samples had dropped to detection limits (22 to 33 ppb); one sample at 60 DAT contained naphthol at 34 ppb. The report concluded that once carbaryl degrades to 1-naphthol, the degradate appears to readily leave the sediment. It did not however, allow for the fact that the degradate could have been present in deeper reaches of the sediment. At adjacent sites, 1 naphthol ranged as high as 120 ppb 2 DAT and then dropped to below detection limits for the remaining sample periods.

Carbaryl residues in pore water were only detected 60 DAT and ranged from 0.57 to 1.15 ppb. It is difficult to understand though how the limit of detection for pore water was so much lower than that for sediment. Carbaryl was only detected in one sediment pore water sample collected from an adjacent site; the residue was close to the limit of detection at 0.05 ppb.

Analyses of sediment grain size and total organic carbon revealed that the clay-silt fraction of the post spray sites ranged from 25% to 73% while TOC ranged from 0.58% to 2.07%. Grain size and TOC were strongly correlated (Pearson R^2 range 0.89 - 0.96); however, there was no correlation between carbaryl residues and TOC.

The study concludes that carbaryl is clearly persistent in treatment areas with residues being detected up to 60 DAT. Additionally, residues in sites adjacent to treated areas indicate that drift does occur. Drift to nontarget sites was attributed to wind, depth of water sampled, and both surface and bottom water currents. Additionally, sediment pore water concentrations exceeded the National Academy of Sciences and Engineering water quality recommendation for carbaryl of 0.06 ppb. Additionally, historic sampling revealed that water column concentrations prior to application ranged as high as 9.2 ppb. The report notes that QA/QC standards suggested that actual pore water concentrations may be higher than those reported. It is uncertain how much naphthol was present in the water column; however, given that naphthol is more toxic than the parent, the potential affect of the residues on aquatic animals is a legitimate concern.

Finally the report compares the sediment residue data to available toxicity data on carbaryl and concludes that Dungeness crab larvae exposed to carbaryl at concentrations ranging from 0.1 to 10 ppb for 25-days exhibited both molting effects and mortality. Although no formal data were provided on the numbers of organisms affected; the author reports that marine fish and invertebrate mortality was observed 2 DAT. The author proposes that the incidental kills could serve as forage for other fish and foraging birds that would then bioaccumulate carbaryl in their tissues. The report further suggests that indirect effects, such as endocrine disruption and mutagenicity, are not sufficiently characterized and that coupled with direct effects and the potential for bioaccumulation in the food chain, carbaryl and 1-naphthol have the potential to impact threatend and/or endangered salmon stocks.

The study would have been more thorough had water column concentrations of carbaryl been measured. Given that the compound was applied using both aerial and hand-held sprayers, it is difficult to assess the affect of drift relative to application method. It would have also been helpful to know how representative the areas sampled were of the total areas treated in terms of TOC and grain size. Additionally, the limit of detection (25 - 35 ppb) was not sufficiently low to document residues in sediment and pore water that may have been sufficiently high to effect benthic invertebrates.

2) Chemicals of Special Concern in Washington State

Report published by the Washington Department of Ecology provides a brief overview of the environmental fate and effects of carbaryl. Although the overview has footnote numbers, no references were provided; therefore, data supporting carbaryl's characterization could not be verified. The report implies that carbaryl is relatively persistent and that recoveries of aquatic systems exposed to carbaryl have taken as long as 3 years. According to the overview, carbaryl is teratogenic, immunosuppressive, and degrades to carcinogenic compounds.

3) Washington Department of Ecology Review of Data Relevant to the Envrionmental Effects of Applying Carbaryl to Control Burrowing Shrimp in Willapa Bay and Grays Harbor Oyster Beds (1987).

The object of the Washington Department of Ecology review was to answer the following questions:

- How long do carbaryl and its primary hydrolysis product 1-naphthol persist in the water column?
- What concentrations of carbaryl and 1-naphthol in water are toxic to marine organisms?
- How long do carbaryl and 1-naphthol persist in the sediments?
- What concentrations of carbaryl and 1-naphthol in sediment are toxic to marine organisms?
- What are the effects on abundance and diversity of infauna?
- What are the effects on abundance and diversity of epifauna?
- What mortality is experienced by Dungenees crab and how does this affect the fishery?
- What mortality is experienced by fish?
- Are birds adversely affected?
- What are the potential ecological impacts of Sevin applications?

While the environmental fate studies on water column and sediment concentrations during and after application of carbaryl showed a decline in carbaryl and 1-naphthol concentrations, much of the data were discounted due to poor detection limits and procedural deficiencies. Open literature reviews of ecological effects revealed that carbaryl is more toxic to crustaceans than to molluscs or fish; however, the degradate 1-naphthol is less toxic to crustaceans than carbaryl but more toxic than the parent to molluscs and fish. Subacute effects of carbaryl were reported at concentrations below the detection limit (1 mg/L) of most of the monitoring studies reported; the report states that circumstantial evidence suggests the potential for toxic effects at or below 0.1 mg/L in sediment. Sublethal effects included reduced development of oysters and delayed molting of crab larvae, malformations in fish eggs and adults. Toxicity of carbaryl is reported to increase with temperature.

Although the report fails to conclusively resolve whether carbaryl and its 1-naphthol degradate are sufficiently persistent to effect aquatic life, it notes that the target population of burrowing shrimp take a number of years to recover. However, failure of a treated area to recover may be due to a number of factors and may not result exclusively on the toxicity of carbaryl or its degradate.

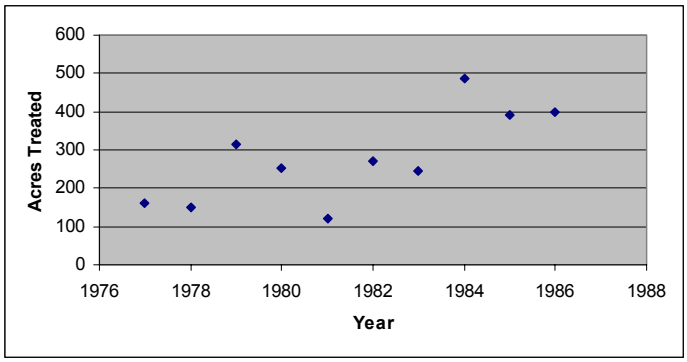

Figure 2. Number of acres treated with carbaryl in Willapa Bay over years.

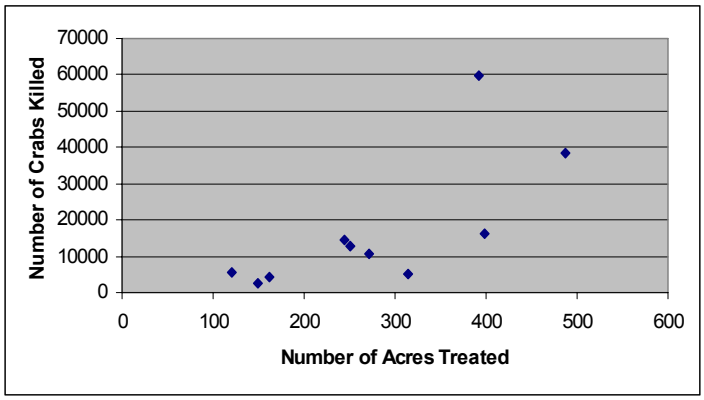

Figure 3. Number of crabs killed versus number of acres treated with carbaryl in Willapa Bay.

Fisheries data collected on Willapa Bay from 1977 to 1986 show (**Figure 2**) that the number of acres treated with carbaryl increased each year. And that the number of crabs killed by carbaryl treatment also increased (**Figure 3**) as the number of acres treated increased. The number of crabs killed was significantly correlated (Pearson Correlation coefficient = 0.72; p > rho = 0.0187) with the number of acres treated. Over the observation period an average of 53 crabs (standard error = 13) were killed per acre. Follow-up studies by the University of Washington that [Dungeness] crab in treated areas are impacted but that further studies are required to establish population-level effects in Willapa Bay.

Mortalities to fish were limited to small specimens which were entrapped in shallow pools by the outgoing tide and directly exposed to carbaryl during treatment; however, the reviewed literature did not address the potential for indirect mortality.

Although no studies were conducted, the report concluded that likelihood of acute or chronic effects of carbaryl on birds was remote.

Whether there are broad ecological impacts associated with the use of carbaryl to control burrowing shrimp in Willapa Bay remains an uncertainty. The Environmental Impact Statement concluded that the use of carbaryl by the commercial oyster industry was not expected to cause significant impacts on the estuarine ecosystem when applied at current levels. It based this conclusion on the fact that:

- Carbaryl is not accumulated by any food chain component or transmitted to higher levels in the food chain.
- No chemically active radical group remains to contaminate the estuarine environment.
- Only a small percentage of the total intertidal lands are treated annually; 0.8% in Willapa Bay and 0.3% in Grays Harbor.

The report recommends though that further work be conducted to evaluate the persistence of carbaryl and 1-naphthol in sediment and to better document the effects of nontarget mortality.

4) Burrowing Shrimp Integrated Pest Management Memorandum of Agreement

The memorandum of agreement (MOA) was established between the Washington State Department of Ecology, Washington State Department of Agriculture, the Washington State Commission on Pesticide Registration, the Washington Department of Fish and Wildlife, the Willapa/Grays Harbor Oyster Growers Association, the Pacific Coast Shellfish Growers Association and the Pacific Shellfish Institute. The agreement acknowledges that while carbaryl and its 1-naphthol degradate affect nontarget species, are likely transported several hundred yards offsite by tidal action, and may persist for several weeks in the water column and sediments within Willapa Bay/Grays Harbor, treatment for burrowing shrimp is necessary if economic losses due to diminished oyster harvests are to be avoided. The agreement acknowledges that additional data on the environmental fate and effects of carbaryl are necessary and that alternative methods of control should be explored to mitigate adverse effects especially on threatened/endangered salmonids. The MOA establishes a process and time for the development of a "sustainable site-specific, environmentally sound and ecologically based [integrated] pest management plan for the control of burrowing." The MOA outlines criteria to be met, i.e., demonstration that burrowing shrimp populations have reached a size sufficient to inflict economic losses, before which carbaryl can be applied.

5) Carbaryl Concentrations in Willapa Bay and Recommendations for Water Quality Guidelines.

In the summer of 2000, the Washington State Department of Ecology initiated a study of Willapa Bay. The study was a follow-up on the Stonic (1999) study from 1996 to 1997 and concern that carbaryl persisted at a level of 0.7 ug/L. The objectives of the study were to:

- determine if there is a carbaryl background that persists in Willapa Bay water outside the July to August spray period;
- analyzie carbaryl in other potential sources to Willapa Bay;
- achieve quantitation limits for carbaryl sufficiently low to evaluate the potential for causing toxicity to sensitive marine organisms;
- review the literature on carbaryl's effects on marine organisms and evaluate appropriate water quality guidelines for carbaryl in Willapa Bay.

Results from the study show that carbaryl was frequently detected in Willapa Bay up to 4 days after application to oyster beds and that carbaryl was transported several miles from the site of application. However, the study showed no evidence of carbaryl background in the Willapa Bay water column. Additionally, tributaries and cranberry bog drainages were not significant carbaryl sources. Carbaryl had dropped to levels below quantitation (0.004 ug/L) approximately 1 month after application

Based on a review of toxicity data on 35 marine species, the report recommended 0.06 ug/L as a probable safe level for marine organisms and a range of 0.1 to 0.7 ug/L as a potential effects threshold. The value of 0.06 ug/L was based on a National Academy of Science approach using an EC50 of 6 ug/L for inhibiting molting in Dungeness crab larvae divided by a 100X safety factor. The data collected from open literature suggests that carbaryl is more toxic to crustaceans and echinoderms than to fish, molluscs, or polychaetes. The study notes that while similar information was not collected on the 1 naphthol degradate, one study has shown it to be roughly twice as toxic to fish as the parent compound but less toxic to crustaceans. Carbaryl was detected at concentrations within the proposed potential effects threshold several miles from treatment areas up to several days following application. The report recommended that future water quality monitoring focus on the period during or immediately after carbaryl applications and that data are collected on carbaryl's 1-naphthol transformation product. Additionally, the report recommends that future effects testing include more sensitive test species and indigenous aquatic species that serve as prey for endangered/threatened species

References

Stonic, Cynthia. 1999. Screening Survey of Carbaryl (Sevin™) and 1-naphthol Concentrations in Willapa Bay Sediments. Washington State Department of Ecology. Publication No. 99-323.

Johnson, Art. 2001. Carbaryl Concentrations in Willapa Bay and Recommendations for Water Quality Guidelines. Washington State Department of Ecology. Environmental Assessment Program. Publication No. 01-03-005.